Nucleophilic Addition of Amines to the Activated Ethylene Bond. Part 3.[1]
Kinetics and Mechanism of the Addition of Amines to *trans*-(2- Furyl)nitroethylene

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The kinetics of addition of a number of primary and secondary aliphatic amines to *trans*-(2-furyl)-nitroethylene in acetonitrile at 25 °C have been studied. It has been shown that the reaction is catalysed both by the amine reagent and by tertiary amines and in the case of primary amines the dependence of the observed second-order rate constant (k_{obs}) on amine concentration takes the form of a hyperbola. The Arrhenius activation energy has been found to be negative for the catalytic reaction route. On the basis of analysing the observed kinetic regularities a stepwise reaction mechanism has been proposed which involves formation of the zwitterionic addition complex (**1**) at the first equilibrium step (k_1, k_{-1}) which is then converted into the reaction product by means of proton transfer in parallel routes, *i.e.* the non-catalytic one (k_2) and that catalysed by the initial (k_3) or tertiary (k_4) amine. The rate constants of the non-catalytic [$k = k_1k_2/(k_{-1} + k_2)$] and catalytic [$k_b = k_1k_3/(k_{-1} + k_2)$] reaction routes have been determined for a number of proton-containing amines; for primary amines the nucleophilic attack rate constants (k_1) and relations for the constants of conversion of the zwitterionic intermediate (**1**) into the reaction product and the disintegration of the former into initial compounds (k_2/k_{-1} and k_3/k_{-1}) have been determined. A mechanism for proton transfer in the intermediate (**1**) is discussed.

A mechanism for addition of charged nucleophiles to an activated carbon–carbon double bond was theoretically predicted by Ingold[2] and then experimentally supported by several authors.[3] According to this mechanism, the reaction proceeds stepwise with the rate-limiting step being nucleophilic attack on the alkenic β-carbon (with respect to the activating group) atom and subsequent rapid protonation of a carbanion intermediate. Questions on the kinetics and mechanism of the addition of electroneutral nucleophiles (amines in particular) to the activated alkene, in aprotic solvents especially, are given much less attention in the literature. However, it often happens in this case that interesting kinetic regularities displaying peculiarities in the mechanism are observed. Bernasconi *et al.*[4] in a number of papers gave a detailed examination of the kinetics and mechanism for the addition of amines to the activated alkene in water and water–dimethyl sulphoxide using temperature-jump and stopped-flow techniques.

On studying the kinetics of secondary amine addition to 5-substituted *trans*-(2-furyl)nitroethylenes (Scheme 1) Kada *et*

Scheme 1.
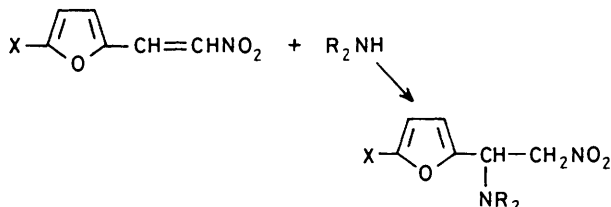
al.[5] came to the conclusion that the reaction is of total second order, *i.e.* first in each of the reactants (though the amine concentration did not vary). When the medium polarity increases the reaction rate declines. Nevertheless, we obtained quite opposite results. As shown previously,[1] piperidine addition to *trans*-(2-furyl)nitroethylene resulting in 2-(1-piperidino-2-nitroethyl)furan, is catalysed in acetonitrile by a second molecule of the same amine and the observed second-order rate constant

k_{obs} (first in each of the reactants) is a linear function of amine concentration ([HN<]) [equation (1)] where k and k_b are the

$$k_{obs} = k + k_b[\text{HN}<] \qquad (1)$$

rate constants of the non-catalytic and catalysed by second amine molecule routes, respectively. Such kinetic relationships are often observed in low-polar media and explained by the participation of amine dimers in the reaction. However, the degree of aliphatic amine self-association in as highly polar a solvent as acetonitrile is negligibly small,[6] and the second-order kinetics can hardly be accounted for by amine dimer attack on *trans*-(2-furyl)nitroethylene. Besides, if catalysis by the initial amine were caused by amine self-association then the effective catalysis (the k_b/k value) should increase as the medium polarity decreases,[7] as the association constant increases in this case. As follows from the data in ref. 1, for ε 37.5–11.6, the decrease in medium polarity results in important rate decreases for both routes (k and k_b). However, the relation k_b/k, is constant. Thus there was a need for more detailed study of the kinetic relationships for the addition of amines to *trans*-(2-furyl)nitroethylene.

Results and Discussion

The Effect of Temperature.—On investigating the effect of temperature on the rate of piperidine addition to *trans*-(2-furyl)nitroethylene, we found that while the non-catalytic route rate (k) accelerates when the temperature rises, the catalytic route rate (k_b) reduces; therefore, the Arrhenius activation energy for the catalytic reaction route is negative (Table 1). This may be accounted for by the presence of a pre-equilibrium step in the reaction, *i.e.* the constants k and k_b (or, at least, the constant k_b) are not the rate constants of an elementary interaction but represent more complex values.

Since this equilibrium, as mentioned above, is not related to a process of amine self-association, we must assume that it refers to the interaction between amine and *trans*-(2-furyl)nitroethyl-

Table 1. Rate constants[a] at various temperatures and activation parameters for the reaction of piperidine addition to trans-(2-furyl)nitroethylene in acetonitrile.

$T/^{\circ}C$	$10^3[HN{<}]^b/mol\ dm^{-3}$	$k/dm^3\ mol^1\ s^{-1}$	$k_b/dm^6\ mol^2\ s^{-1}$	s	r	N
2	0.8—14.1	0.446 ± 0.066^c	$590 + 8^c$	0.137	0.999	9
15	0.8—12.5	0.702 ± 0.030	486 ± 5	0.060	0.999	7
25	1.8—14.1	1.02 ± 0.05	392 ± 7	0.078	0.999	9
40	0.8—14.1	1.62 ± 0.12	318 ± 13	0.097	0.997	6
55	7.0^d—17.0	2.03 ± 0.22	297 ± 19	0.133	0.996	4
70	6.3^d—12.5	4.14 ± 0.08	239 ± 8	0.035	0.999	5
log A		4.27 ± 0.28	0.82 ± 0.12			
$E_A/kJ\ mol^{-1}$		24.4 ± 1.6	$-(10.2 \pm 0.7)$			
r		-0.991	0.991			
$\Delta S^{\ddagger}_{25}/J\ mol^{-1}\ K^{-1}$		$-(172 \pm 5)$	$-(238 \pm 3)$			

[a] s is the standard deviation, r is the correlation coefficient, N is the number of kinetic curves. [b] Variation range of amine concentration. [c] Root-mean-square deviations. [d] The reaction becomes reversible at these temperatures with lower amine concentrations which is indicated by a narrowing of the optical density variation range (the increase of solution absorption after the reaction is completed) and by a decrease of the observed second-order rate constants in the course of the reaction; the k_{obs} values show a positive deviation from relationship (1) plotted for higher amine concentrations.

ene. The high absolute values and the similarity of parameters for the sensitivity to medium polarity of the non-catalytic and catalytic reaction routes [estimated by the Kirkwood equation, $\log k/k_0 = 21.4(\varepsilon - 1)/(2\varepsilon + 1)$ and $\log k_b/k_0 = 17.5(\varepsilon - 1)/(2\varepsilon + 1)$][1] as well as the conclusion about high degree of charge distribution in the transition state, permit an assumption that in both reaction routes there is a zwitterionic tetrahedral intermediate (1). This assumption is also supported by the highly negative values of the activation entropy (Table 1), as solvation of two charged sites must cause substantial entropy
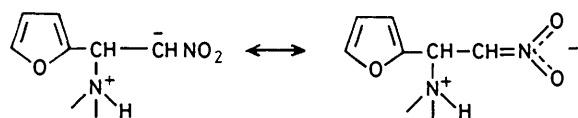
(1)
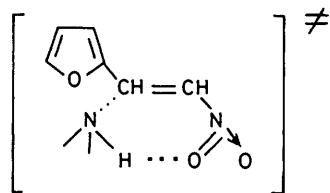
(2)

losses. The alternative explanation of the highly negative values for the activation entropy by formation of the low-polar cyclic transition state (2) is not in agreement with the effect of medium polarity on the rate.

Mechanism.—It was found that for some amines, the dependence of the observed second-order rate constant on amine concentration is not completely linear (Figure 1) and is only described by equation (1) for low amine concentrations. When the amine concentration increases the slope of the dependence of k_{obs} on $[HN{<}]$ decreases regularly (downward curvature). Thus, the data are in accord with a mechanism involving formation of the zwitterionic intermediate (1) in the first equilibrium step with subsequent conversion of the former into the product via proton transfer by two parallel routes, i.e. k_2 and k_3 (Scheme 2).

The application of the steady-state hypothesis to this mechanism gives equation (2):

$$k_{obs} = \frac{k_1(k_2 + k_3[HN{<}])}{k_{-1} + k_2 + k_3[HN{<}]} \quad (2)$$

Calculations of the Rate Constants.—In the framework of Scheme 1, the linear dependence of k_{obs} on amine concentration meets the condition $k_{-1} \gg k_3[HN{<}]$* and the observed second-order rate constant is described by equation (3) which is

$$k_{obs} = \frac{k_1}{k_{-1} + k_2}(k_2 + k_3[HN{<}]) \quad (3)$$

similar to equation (1). Thus, the constants k and k_b are expressed by equations (4) and (5), respectively.

$$k = \frac{k_1 k_2}{k_{-1} + k_2} \quad (4)$$

$$k_b = \frac{k_1 k_3}{k_{-1} + k_2} \quad (5)$$

At $k_{-1} \approx k_3[HN{<}]$ a curvilinear (hyperbolic) dependence of the observed second-order rate constant on the amine concentration occurs according to equation (2). This sort of relationship was obtained for the reactions of primary amines (Figure 1). Treatment of the experimental data took two forms.

Method A. Using equation (1) the values for the constants k and k_b were found as the intercept and slope, respectively, of the linear part of curve (Figure 1) in the region of low amine concentration ($[HN{<}]$). For the reaction of the majority of amines (in which the difference between the constants k_1 and k is not less than one order of magnitude) approximation (6) is

$$\frac{1}{k_{obs} - k} \approx \frac{1}{k_1} + \frac{1}{k_b} \cdot \frac{1}{[HN{<}]} \quad (6)$$

* It is also necessary to meet the condition $k_2 \leqslant k_{-1}$ because when $k_2 \gg k_{-1}$ no catalysis is observed as nucleophilic attack is a rate-limiting step: $k_{obs} = k_1$. In the analysis of a kinetic equation of type (2) the condition $k_{-1} \gg k_2 + k_3[HN{<}]$ is generally obeyed.[8] However, as shown below, the ratio k_2/k_{-1} is rather large in the case of sterically hindered amines for the reaction under investigation (e.g. k_2/k_{-1} 0.455 for t-butylamine) and the condition $k_{-1} \gg k_2 + k_3[HN{<}]$ is not satisfied in contrast to the condition $k_{-1} \gg k_3[HN{<}]$.
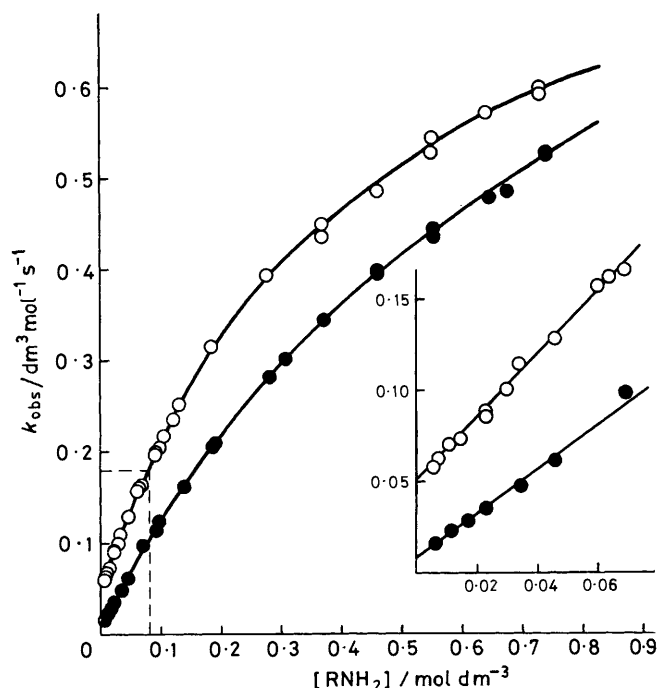
Figure 1. Plots of k_{obs} versus [amines] for the reaction of trans-(2-furyl)nitroethylene with allylamine (●) and cyclohexylamine (○) in acetonitrile at 25 °C.
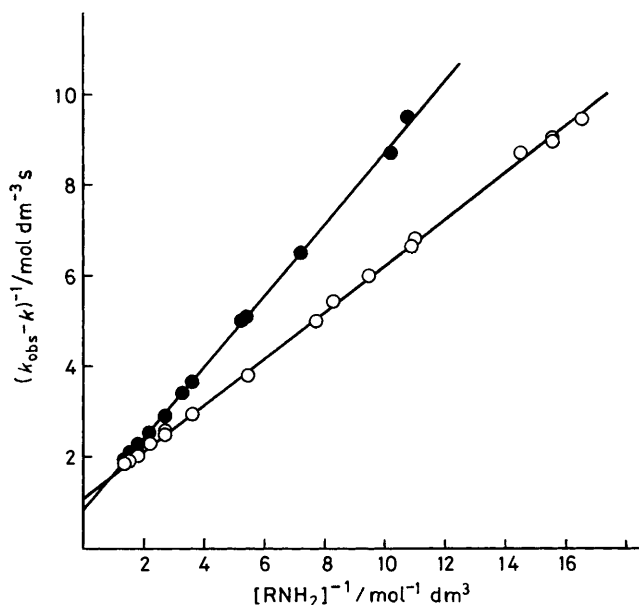

Figure 2. Inverse of the plots in Figure 1, according to approximation (6); ●, allylamine; ○, cyclohexylamine.

quite acceptable* and this can be used to determine the rate constant of amine nucleophilic attack by amine on trans-(2-furyl)nitroethylene, i.e. k_1 (the limit the curve tends to in Figure 1). In this case the curvilinear plots in Figure 1 can be linearized

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* See Appendix.

† k_2 represents intramolecular proton transfer from the nitrogen ammonium atom in intermediate (1) to the carbanion centre or to the oxygen of the nitro group, k_{-1} represents C–N bond breaking in intermediate (1); with the growth of steric hindrance at the nitrogen atom the rate of both processes increases.

by a plot of $1/(k_{obs} - k)$ against $1/[HK<]$ according to equation (6) which is illustrated in Figure 2. Thus, using equations (3)–(6) we determined (Table 2) the constants k, k_b, and k_1 and also the ratios for the rate constants of the conversion of intermediate (1) into the product and disintegration of the latter into the initial compounds [k_2/k_{-1} and k_3/k_{-1}, equation (7) and (8), respectively].

$$\frac{k_2}{k_{-1}} = \frac{k}{k_{-1} - k} \tag{7}$$

$$\frac{k_3}{k_{-1}} = \frac{k_b}{k_1 - k} \tag{8}$$

Method B. When the ratio k_1/k is small (e.g. with steric hindrance increased in the amines) it is advantageous to present equation (2) as the polylinear function (9) in order to determine the constants k, k_b, and k_1:

$$k_{obs} = k + k_b[HN<] - \frac{k_b}{k_1}(k_{obs}[HN<]) \tag{9}$$

The results of the treatment of several amines by equation (9) are given in Table 3, and the values of the constants generally coincide with those obtained by Method A. It should be noted, nevertheless, that the use of equation (9) for sterically unhindered amines is not advantageous as this gives large errors in the determination of k because the ratio k_1/k is large (cf., e.g. the data for allylamine in Table 3).

The Effect of Amine Structure.—The results indicate the effect of the structure of the amines on the interaction with trans-(2-furyl)nitroethylene. The rate constant k_1 for nucleophilic attack is highly resistive to steric hindrance in the amine. Thus, in passing from butylamine to t-butylamine, k_1 decreases 70-fold (Tables 2 and 3). This is indicative of a high degree of C–N bond formation in the transition state of the first step of the reaction.

The effect of the structure of the amines on the ratio of rate constants for the catalytic conversion of intermediate (1) into the product and the disintegration of intermediate (1) into initial compounds (k_3/k_{-1}) is rather small though the general tendency towards decreasing the ratio k_3/k_{-1} with an increase in steric hindrance and a decrease in amine basicity is clear (Tables 2 and 3).

A different and somewhat unexpected picture is observed for the ratio k_2/k_{-1}. When the amine basicity decreases, the value of k_2/k_{-1} (as well as k_3/k_{-1}) slightly decreases (cf. Table 2). The growth of steric hindrance in the amine results in an important increase in the ratio k_2/k_{-1} (almost 30-fold on passing from butylamine to t-butylamine). This fact may be accounted for by the higher sensitivity of k_2 to steric hindrance at the nitrogen ammonium atom in intermediate (1) by comparison with k_{-1},† i.e. when steric hindrance increases a proton is 'expelled' from the ammonium cation.

Catalysis by Tertiary Amines.—The participation of the second molecule of the initial amine in the conversion of intermediate (1) into the product may be explained in terms of general base catalysis. Proton transfer in intermediate (1) from the nitrogen ammonium atom to the carbanion centre may be effected by other bases as well, e.g. by tertiary amines by the k_4 route in parallel to routes k_2 and k_3 (Scheme 3).

Indeed, as seen from Figure 3, the dependence of k_{obs} on triethylamine concentration for the reaction of alkenes (3) with benzylamine is curvilinear (analogous to reaction catalysis by

Table 2. Rate constants for the reaction of amines addition to trans-(2-furyl)nitroethylene in acetonitrile at 25 °C.

No.	Amine	Data processing by equation (1)					
		$10^2[HN<]$/mol dm^{-3}	10^3k/ dm^3 mol^{-1} s^{-1}	$k_b{}^a$/ dm^6 mol^{-2} s^{-1}	$10^3 s$	r	N
1	Ethylamine	0.2—1.9	58.8 ± 5.9	9.95 ± 0.45	7.1	0.9969	5
2	Butylamine	0.3—3.5	60.5 ± 2.4	9.02 ± 0.11	3.3	0.9996	7
3	Isopropylamine	0.9—3.5	43.8 ± 0.6	1.40 ± 0.02	0.47	0.9997	4
4	Cyclohexylamine	0.6—9.2	51.4 ± 1.6	1.67 ± 0.03	3.6	0.9974	16
5	Allylamine	0.6—9.8	8.86 ± 0.68	1.15 ± 0.01	1.21	0.9996	8
6	Benzylamine	1.0—5.9	4.26 ± 0.49	0.87 ± 0.02	0.71	0.9990	9

No.	$10^2[HN<]$/mol dm^{-3}	Data processing by equation (6)								
		$(10/k_4)$ dm^{-3} mol s	$(10^2/k_b)$ dm^6 mol^2 s	s	r	N	k_1/dm^3 mol^{-1} s^{-1}	$k_b{}^a$/dm^6 mol^{-2} s^{-1}	$10^2k_2/k_{-1}$	(k_3/k_{-1}) dm^3 mol^{-1}
1	6—15	2.71 ± 0.41	10.1 ± 0.3	0.036	0.9960	9	3.69	9.93	1.62	2.73
2	3—19	2.68 ± 0.20	10.3 ± 0.1	0.037	0.9994	13	3.74	9.71	1.64	2.64
3	21—56	4.15 ± 0.4	63.2 ± 1.4	0.042	0.9977	12	0.69	1.58	6.77	2.44
4	6—74	11.5 ± 0.4	51.0 ± 0.5	0.119	0.9991	23	0.87	1.96	6.26	2.39
5	9—74	8.87 ± 0.27	77.9 ± 0.6	0.068	0.9996	18	1.13	1.28	0.790	1.14
6	8—32	13.7 ± 0.9	111.5 ± 1.5	0.146	0.9987	15	0.731	0.90	0.586	1.23

^{a} Different regression equations may give somewhat different values for the parameters (k_b).

Table 3. The results of calculations of rate constants for the interaction of amines with trans-(2-furyl)nitroethylene in acetonitrile at 25 °C by equation (9).

No.	Amine	$10^3[HN<]$/ mol dm^{-3}	10^3k/dm^3 mol^{-1} s^{-1}	10^2k_b/dm^3 mol^{-2} s^{-1}	(k_b/k_1) dm^3 mol^{-1}	$10^4 s$	R^a	N	k_1/dm^3 mol s^{-1}	$10^2k_2/k_{-1}$	(k_3/k_{-1}) dm^3 mol^{-1}
1	t-Butylamine	85—1 365	16.8 ± 0.1	4.85 ± 0.12	0.903 ± 0.032	1.2	0.9998	8	0.0537	45.5	1.31
2	t-Octylamine	110—884	7.08 ± 0.07	0.87 ± 0.11	0.51 ± 0.11	0.41	0.9998	6	0.0171	70.7	0.87
3	Isopropylamine	8—560	42.3 ± 2.7	177 ± 4	2.51 ± 0.10	65	0.9986	32	0.706	6.37	2.67
4	Cyclohexylamine	6—735	45.6 ± 2.4	217 ± 5	2.40 ± 0.07	63	0.9993	27	0.903	5.32	2.53
5	Allylamine	6—740	9.0 ± 3.2	130 ± 3	1.16 ± 0.06	73	0.9990	25	1.11	0.817	1.18

^{a} R is the multiple correlation coefficient.
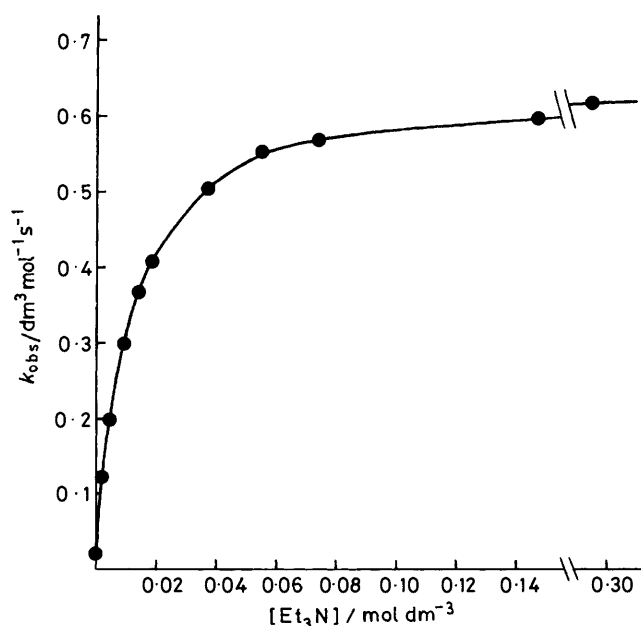
Figure 3. Plot k_{obs} versus [triethylamine] for the reaction of trans-(2-furyl)nitroethylene with benzylamine ([PhCH$_2$NH$_2$] 0.0163 mol dm^{-3}) in acetonitrile at 25 °C.

initial amine; see Figure 1) reaching a plateau (which corresponds to the nucleophilic attack rate constant k_1) when the
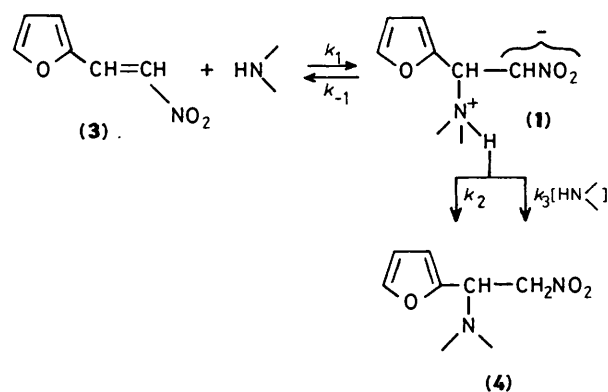
Scheme 2.

triethylamine concentration increases. Similar dependences are also observed for the reaction of secondary amines in the presence of tertiary amines as catalyst* (Figure 4) which confirms the identity of the reaction mechanism for primary and secondary amines with trans-(2-furyl)nitroethylene.

Application of the steady-state hypothesis to Scheme 3 gives equation (10).

* In contrast to catalysis by the reacting amine of the addition of secondary amines to trans-(2-furyl)nitroethylene where the dependence of k_{obs} on [HN<] is linear for the total range of secondary amine concentration ([HN<] ≯ 1–1.5 mol dm^{-3}).
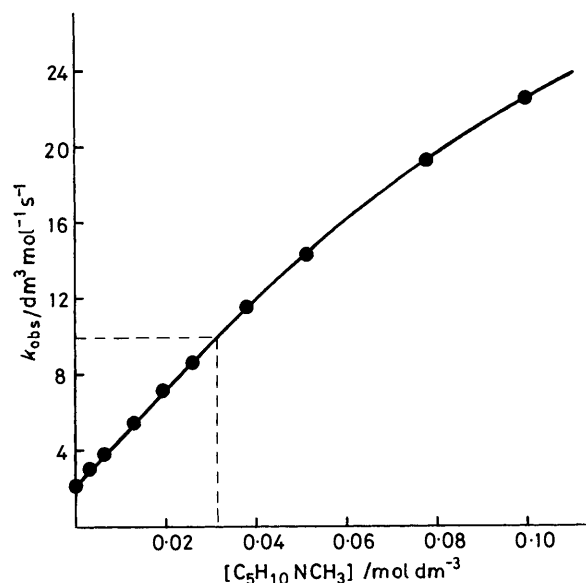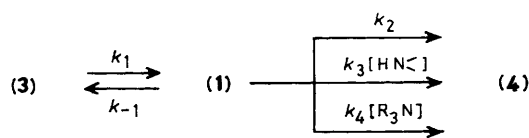
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Figure 4. Plot of k_{obs} versus [N-methylpiperidine] for the reaction of *trans*-(2-furyl)nitroethylene with piperidine ([$C_5H_{10}NH$] 0.002 96 mol dm^{-3}) in acetonitrile at 25 °C.

Scheme 3.

$$k_{obs} = \frac{k_1(k_2 + k_3[HN<] + k_4[R_4N])}{k_{-1} + k_2 + k_3[HN<] + k_4[R_3N]} \quad (10)$$

This expression describes the reaction rate of primary amines with *trans*-(2-furyl)nitroethylene in the presence of tertiary amines in acetonitrile. For secondary amines with low [R_3N] a linear dependence of k_{obs} on [R_3N] is observed (Figure 4) which complies with the condition $k_{-1} \gg (k_3[HN<] + k_4[R_3N])$. The catalytic rate constant for the reaction route with the participation of tertiary amine (k_m) may be found by the slope of this dependence defined by equation (11). For the dependence shown in Figure 4, $k_m = 256 \pm 2.6$ dm^6 mol^{-2} s^{-1}.

$$k_m = \frac{k_1 k_4}{k_{-1} + k_2} \quad (11)$$

Mechanism of Proton Transfer in Intermediate (1).—The mechanism of proton transfer in the zwitterionic intermediate (1) is intriguing and important. This problem closely approaches that of the base catalysis mechanism in nucleophilic vinylic substitution by amines for sluggish leaving groups.[9,10] An earlier interpretation of such base catalysis by Rappoport *et al.*[9] was in terms of a rapid equilibrium deprotonation of the zwitterionic adduct followed by rate-limiting, general-acid-catalysed leaving group departure from the carbanionic adduct. In their most recent study Rappoport and Peled[10] prefer a mechanism whereby proton transfer from zwitterion to base is rate limiting. A similar problem also arises in nucleophilic aromatic substitution, and Bernasconi *et al.*[11] discussed the problem of proton transfer in Meisenheimer complexes formed from activated aromatic compounds and amines. Several facts were presented to prove that proton transfer from Meisenheimer complexes might be rate

limiting in some cases. Bernasconi *et al.* also observed rate-limiting proton transfer from zwitterionic intermediate to the base in amine addition to 1,1-diphenyl-2,2-dinitroethylene,[4a] benzylidenemalononitrile,[4b] α-cyano-4-nitrostilbene, and α-cyano-2,4-dinitrostilbene[4c] in the 1:1 Me_2SO–H_2O (v/v).

The transition state of the second step of the reaction in question has structure (5) for the catalytic route, and proton transfer catalysed by the base (B) is represented by Scheme 4.
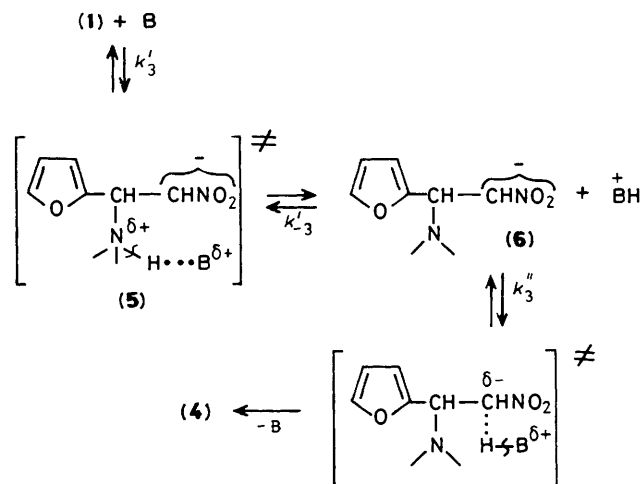
Scheme 4.

When the protonation rate of the carbanionic centre in intermediate (6) exceeds the protonation rate of the amino nitrogen atom ($k_3'' \gg k_{-3}'$), deprotonation of intermediate (1) is a rate-limiting step of proton transfer, *i.e.* $k_3 = k_3'$. If $k_{-3}' \gg k_3''$ the rate constant for catalytic proton transfer designated as k_3 in Scheme 2 is defined by the expression $k_3 = k_3'k_3''/k_{-3}'$. These two situations are kinetically equivalent.

Two alternatives are possible for the non-catalytic proton transfer in intermediate (1) by k_2 route: (i) intramolecular proton transfer to the carbanion centre *via* a four-membered ring and (ii) proton transfer to the nitro oxygen atom a six-membered ring with the formation of the *aci*-nitro compound subsequently converted into product (4). We hope to give more detailed answers to these questions.

Experimental

Purification of Materials.—Acetonitrile[12] and *trans*-(2-furyl)nitroethylene[1] for kinetic measurements were purified as described previously. Primary and secondary amines were rectified three times over sodium and a medium fraction was taken (benzylamine was recrystallized twice in the form of the oxalate from water, inserted into free base by potassium hydroxide, and rectified over sodium under vacuum); their characteristics agreed with the data given in the literature. Triethylamine and N-methylpiperidine were distilled over sodium and treated with tosyl chloride to remove impurities. The mixture was filtered, a small quantity of water was added to destroy the tosyl chloride, the amine was distilled, rectified twice over sodium, and a medium fraction was taken.

Kinetics Measurements.—The kinetics of the reaction were studied spectrophotometrically by the decrease of the optical densities of initial substrate (3) at 350 nm under pseudo-first-order conditions (excess of amine). A SF-26 spectrophotometer (LOMO; U.S.S.R.) was used with 1.00 cm silica cells. The kinetic method is given in Part 2.[1]

The observed second-order rate constants (k_{obs}) at the

Table 4. The results of data processing for the addition of amines to *trans*-(2-furyl)nitroethylene in acetonitrile (25 °C) by equation (12).[a]

No.	Amine	$10^2[HN<]/$ mol dm^{-3}	$(10/k_1)/$ mol dm^{-3} s	$(10^2 k_b)$ mol^2 dm^{-6} s	s	r	N	$k_1/$ dm^3 mol^{-1} s^{-1}	$k_b/$ dm^6 mol^{-2} s^{-1}
1	Cyclohexylamine	6—74	10.8 ± 0.4	48.2 ± 0.4	0.106	0.9992	23	0.924	2.07
2	Allylamine	9—74	8.80 ± 0.27	77.4 ± 0.6	0.068	0.9996	18	1.14	1.29

[a] The initial k_1, k, and k_b data are taken from Table 2.

various concentrations of amine are available in Supplementary Publication No. SUP 56734 (11 pp.).*

Appendix

Using standard mathematical procedure, equation (2) may be transformed into (12), which is a strict equality, in contrast to

$$\frac{1}{k_{obs} - k \dfrac{k_1}{k_1 + k_b[HN<]}} = \frac{1}{k_1} + \frac{1}{k_b} \cdot \frac{1}{[HN<]} \quad (12)$$

approximation (6). This equation may be used to verify the applicability of approximation (6) and/or ascertain the constants k_1 and k_b (as well as the ratios k_2/k_{-1} and k_3/k_{-1}). With this end in view an iteration procedure using equation (12) was performed by substituting the approximate values of k_1 and k_b determined using equation (6) into the left-hand side of equation (12) (Table 2). However, even the first iteration cycle for all the amines adduced in Table 2 ($k_1 > 10k$) gives k_1 and k_B values coinciding within error with those calculated by equation (6) (see Table 4). This proves that approximation (6) is fulfilled with satisfactory accuracy.

* For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1989, Issue 1.

References

1 Part 2, I. F. Perepichka, L. I. Kostenko, A. F. Popov, and A. Ju. Chervinski, *Zh. Org. Khim.*, 1988, **24**, 822.

2 C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Bell, London, 1953, p. 690.

3 M. J. Kamlet and D. J. Glower, *J. Am. Chem. Soc.*, 1956, **78**, 4556; B.-A. Feit and A. Zilkha, *J. Org. Chem.*, 1963, **28**, 406; B.-A. Feit, J. Sinnreich, and A. Zilkha, *ibid.*, p. 3245; W. G. Davies, E. W. Hardisty, T. P. Nevell, and R. H. Peters, *J. Chem. Soc. B*, 1970, 998.

4 (a) C. F. Bernasconi and D. J. Carré, *J. Am. Chem. Soc.*, 1979, **101**, 2698; (b) C. F. Bernasconi, J. P. Fox, and S. Fornarini, *ibid.*, 1980, **102**, 2810; (c) C. F. Bernasconi and S. Fornarini, *ibid.*, p. 5329; (d) C. F. Bernasconi, C. J. Murray, J. P. Fox, and D. J. Carré, *ibid.*, 1983, **105**, 4349; (e) C. F. Bernasconi, R. A. Renfrow, and P. R. Tia, *ibid.*, 1986, **108**, 4541; (f) C. F. Bernasconi and C. J. Murray, *ibid.*, p. 5251.

5 R. Kada, V. Knoppová, J. Kováč, and I. Maleňáková, *Collect. Czech. Chem. Commun.*, 1984, **49**, 2496.

6 C. S. Springer and D. W. Meek, *J. Phys. Chem.*, 1966, **70**, 481.

7 L. M. Litvinenko and N. M. Olejnik, 'Mechanisms of the Actions of Organic Catalyst. Base and Nucleophilic Catalysis,' Naukova Dumka, Kiev, 1984, p. 99 (in Russian).

8 Z. Rappoport, *Acc. Chem. Res.*, 1981, **14**, 7; D. R. Palleros and N. S. Nudelman, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1277; N. S. Nudelman and D. R. Palleros, *ibid.*, 1985, 479.

9 Z. Rappoport and R. J. Ta-Shma, *J. Chem. Soc. B*, 1971, 871, 1461; Z. Rappoport and N. J. Ronen, *J. Chem. Soc., Perkin Trans. 2*, 1972, 955; Z. Rappoport and P. Peled, *ibid.*, 1973, 616; Z. Rappoport and A. Topol, *ibid.*, 1975, 863.

10 Z. Rappoport and P. Peled, *J. Am. Chem. Soc.*, 1979, **101**, 2682.

11 C. F. Bernasconi and C. L. Gehriger, *J. Am. Chem. Soc.*, 1974, **96**, 1092; C. F. Bernasconi and F. Terrier, *ibid.*, 1975, **97**, 7458; C. F. Bernasconi, C. L. Gehriger, and R. H. de Rossi, *ibid.*, 1976, **98**, 8541; C. F. Bernasconi, R. H. de Rossi, and P. Schmid, *ibid.*, 1977, **99**, 4090; C. F. Bernasconi, *Acc. Chem. Res.*, 1978, **11**, 147.

12 L. I. Kostenko, A. F. Popov, V. V. Kravchenko, I. F. Perepichka, *Zh. Org. Chim.*, 1986, **22**, 245.